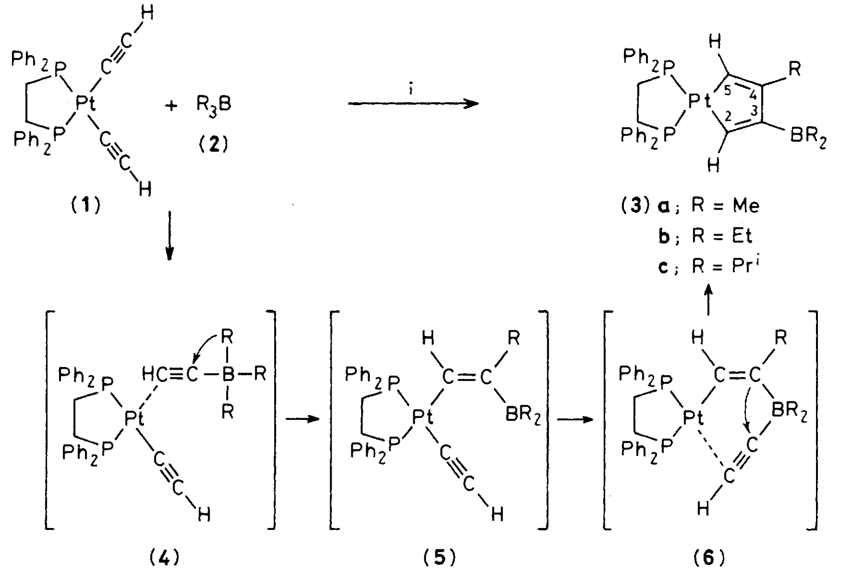
Synthesis of Platinacyclopentadienes *via* Organoboration of *cis*-Platinum(II) Acetylides

Angelika Sebald and Bernd Wrackmeyer*

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 München 2, West Germany

Platinacyclopentadienes are obtained in high yield from the reaction between trialkylboranes R_3B (R = Me, Et, Pr^i) and *cis*-1,2-bis(diphenylphosphino)ethanediethynylplatinum(II) as the result of two consecutive 1,1-organoboration reactions.

The potential of metallacyclopentadienes in synthesis is well recognized.[1,2] So far platinacyclopentadienes have been described only with aryl or ester substituents[3] or as intermediates[4] and a convenient synthesis of these compounds is clearly desirable. Bearing in mind the results of the organoboration of bis(alkynyl)stannanes[5,6] and the recent success in the 1,1-organoboration of *trans*-bis(alkynyl)platinum(II) compounds[7] we have now studied the reaction between *cis*-1,2-bis(diphenylphosphino)ethane (dppe)-diethynylplatinum(II) (**1**) and trialkylboranes (**2**). The reaction proceeds according



Scheme 1. *Reagents and conditions:* i, in CH_2Cl_2 or CD_2Cl_2 between −78 and 30 °C; the compounds (**3a**—**c**) are formed using either a stoicheiometric amount or an excess of R_3B.

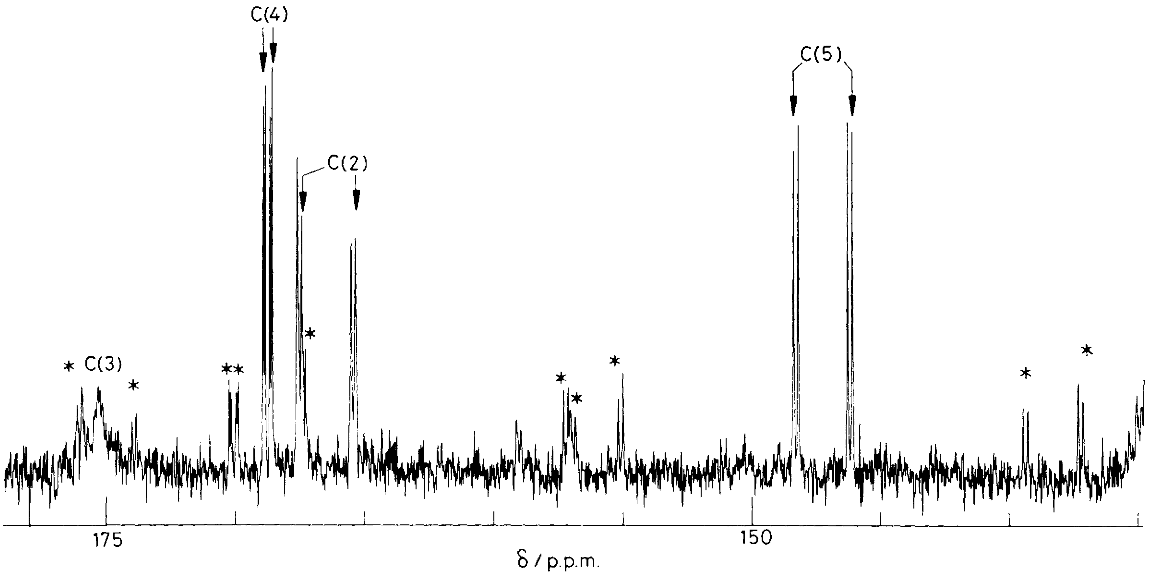


Figure 1. 50.3 MHz ^{13}C N.m.r. spectrum with ^{1}H broad band decoupling of (**3b**) showing the ^{13}C resonances of the olefinic carbons. The assignment is based (i) on the relative magnitude of J (^{195}Pt, ^{13}C) (peaks denoted by *) [C (2, 4, 5)], (ii) on the line-width [C(3)], (iii) on substituent effects of R in (**3a**—**c**) [C(2, 4, 5)], and (iv) on the splitting due to J (^{13}C, ^{1}H) in the proton coupled ^{13}C n.m.r. spectrum [C(2, 4, 5)].

to Scheme 1 and the platinacyclopentadienes (**3**) are obtained in quantitative yield. The compounds (**3**) are yellow to dark yellow solids, which decompose at *ca.* 55—60 °C before melting. They are extremely air- and moisture-sensitive and storage in the dark is advisable.

The proposed mechanism given in Scheme 1 involves the cleavage of the Pt–C≡ bond leading to an alkynylborate-like intermediate (**4**). Electrophilic attack of platinum at the C≡C bond accompanied by a 1,2-shift of an R group gives compound (**5**). Complex (**5**) is not observed (in contrast with the corresponding *trans*-Pt^{II} compound[7]) but a rapid intramolecular reaction leading to another alkynylborate-like intermediate (**6**) is believed to take place. From (**6**) a 1,2-shift of the olefinic group gives the title compounds (**3**).[†]

The reactions between (**1**) and (**2**) are readily monitored by i.r. and ^{1}H, ^{11}B, ^{31}P, and ^{195}Pt n.m.r. spectroscopy. All n.m.r. data are fully in accord with the structure of (**3**).[‡] Particularly noteworthy are the ^{13}C resonances of the olefinic carbon atoms of the platinacyclopentadiene ring in the ^{13}C n.m.r. spectra [Figure 1].

Recently a convenient synthesis has been developed for (**1**)[8] and procedures for the preparation of (**2**) are well established.[9,10] Therefore, this novel and highly efficient route to platinacyclopentadienes (**3**) shows great promise for further studies of this type of compound.

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[†] Alternative reaction pathways are possible depending on the reactivity of the Pt–C≡ bond in the intermediate complex (**5**) and on the nature of R_3B. This has been observed for the compounds *cis*-[Pt(C≡C–R)$_2$(PR$'_3$)$_2$], R ≠ H, where various types of platinum(0)–cyclobutadiene complexes are formed. The results will be reported in a full paper.

[‡] Representative n.m.r. data (Bruker WP 200) for (**3**), 0.4 M in [^{2}H$_2$]methylene chloride at 28 °C; chemical shifts for ^{1}H, ^{11}B, ^{13}C, ^{31}P, and ^{195}Pt relative to internal Me$_4$Si, external BF$_3$·OEt$_2$, external Me$_4$Si, external 85% H$_3$PO$_4$, and Ξ(^{195}Pt) = 21.4 MHz, respectively. Coupling constants J/Hz to ^{195}Pt are given in parentheses and those to ^{31}P in square brackets: (**3a**): δ(^{31}P) 48.9 (1779.8) [6.1], 49.0 p.p.m. (1778.5) [6.1]; δ(^{11}B) 77.1 p.p.m. (br.); δ(^{195}Pt) −436.4 p.p.m.; δ(^{13}C) 175.1 (853.3) [103.3, 7.6] C(2), 174.7 (br.) C(3), 162.2 (133.2) [11.2, 3.4] C(4), 149.7 p.p.m. (885.0) [105.6, 8.2] C(5); δ(^{1}H) 8.30 (108.2) [11.5, 11.5] PtC(2)(H)=, 6.80 (111.0) [11.0, 9.5] PtC(5)(H)=. (**3b**): δ(^{31}P) 48.6 (1777.4) [6.1], 49.1 p.p.m. (1782.0) [6.1]; δ(^{11}B) 77.7 p.p.m. (br.); δ(^{195}Pt) −434.9 p.p.m.; δ(^{13}C) 166.4 (854.6) [105.0, 8.3] C(2), 175.3 (br.) C(3), 168.8 (132.2) [13.4, 3.8] C(4), 147.2 p.p.m. (898.0) [143.0, 8.9] C(5); δ(^{1}H) 7.85 (108.2) [11.5, 11.5] PtC(2)(H)=, 6.97 (112.0) [9.9, 9.9] PtC(5)(H)=. (**3c**): δ(^{31}P) 48.0 (1779.8) [6.1], 49.4 p.p.m. (1794.4) [6.1]; δ(^{195}Pt) −428.6 p.p.m.; δ(^{13}C) 154.2 (851.0) [107.0, 7.6] C(2), 176.2 (br.) C(3), 174.8 (138.5) [14.1, 4.1] C(4), 145.3 p.p.m. (913.2) [107.4, 8.8] C(5).